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DISCOVERY OF METEORITIC LAKARGIITE ($CaZrO_3$), A NEW ULTRAREFRCTORY MINERAL FROM THE ACFER 094 CARBONACEOUS CHONDRITE

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Introduction: During a nano-mineralogy investigation of the Acfer 094 carbonaceous chondrite, lakargiite ($CaZrO_3$) was identified as submicrometer inclusions in an isolated hibonite grain in section USNM 7233-1. The hibonite grain is described in Simon and Grossman [1]. Lakargiite is a recently found perovskite-group mineral from high-temperature skarns in ignimbrites of the Upper-Chegem volcanic structure, the North Caucasus, Russia [2]. Reported here is the first extraterrestrial occurrence of lakargiite, as a new ultrarefractory mineral in a primitive meteorite, among the first solids formed in the solar system. Field-emission SEM with EDS and electron back-scatter diffraction (EBSD) was used to characterize its composition and structure and associated phases.

Occurrence, Chemistry, and Crystallography: Lakargiite [$Ca_{0.95}(Zr_{0.87}Ti_{0.16})O_3$] occurs along with tazheranite [$(Zr_{0.52}Ti_{0.18}Ca_{0.16}Y_{0.06}Fe_{0.05}Sc_{0.03})O_{1.75}$], Zr-bearing perovskite [$Ca_{0.94}(Ti_{0.98}Zr_{0.06})O_3$] and Os-W-alloy [$Os_{0.81}W_{0.13}Fe_{0.06}$] as fine-inclusions scattered in the central area of the hibonite [$Ca(Al_{11.70}Ti_{0.14}Fe_{0.10}Mg_{0.06})O_{19}$] grain (Fig. 1). Lakargiite appears as irregular or subhedral lath-shaped grains, 300–900 nm in size, sometimes in contact with Os-W or perovskite. Associated tazheranite is a Ca-stabilized cubic zirconia (CSZ), likely being the first reported meteoritic CSZ. EBSD analysis revealed that the lakargiite has a perovskite *Pbnm* structure, identical to that of synthetic $CaZrO_3$ [3], showing a = 5.591 Å, b = 5.762 Å, c = 8.017 Å, V = 258.3 Å^3, Z = 4.

Origin and Significance: Lakargiite is a new Zr-dominant ultrarefractory mineral, joining the Zr-rich refractory minerals allendeite ($Sc_4Zr_3O_{12}$) [4], tazheranite (Sc- or Y- stabilized cubic zirconia) [4, 5] and panguite [6]. Texturally, lakargiite, tazheranite, Zr-bearing perovskite and Os-W formed before host hibonite. Lakargiite is likely an early condensate. Further work is under way to determine its place in the nebula.

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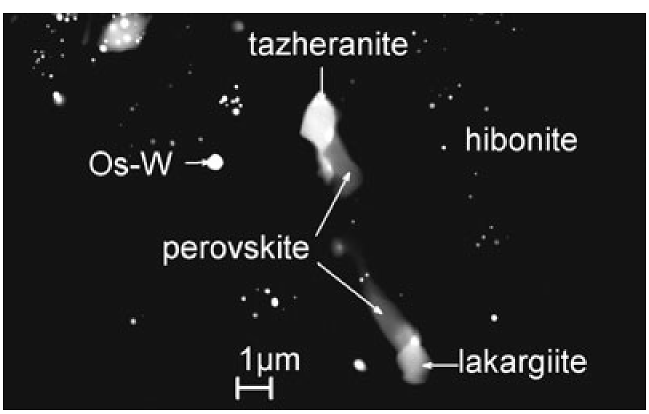

Fig 1. BSE image showing lakargiite in Acfer 094.

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THORTVEITITE ($Sc_2Si_2O_7$), THE FIRST SOLAR SILICATE?

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Introduction: In condensation calculations for a cooling gas of solar composition, or dust enriched variants, melilite is invariably the earliest condensing silicate except at very high dust-to-gas ratios [e.g., 1]. The possibility that silicates of the highly refractory lithophiles, such as Sc and Zr, actually form first is not tested because of a lack of thermodynamic data. Meteoritic occurrences may, therefore, provide the best clues to the earliest evolution of Si in nebular solids. During a nano-mineralogy investigation of the Murchison CM2 carbonaceous chondrite, we identified thortveitite ($Sc_2Si_2O_7$), along with davisite ($CaScAlSiO_6$), panguite [$(Ti,Sc,Al,Mg)_{1.8}O_3$], spinel, and Sc-rich diopside, in the Sc-enriched ultrarefractory inclusion MUR1. This is the first meteoritic occurrence of thortveitite and the second natural occurrence of panguite, a Ti-rich oxide recently discovered in Allende [2]. Field-emission SEM with EDS, electron back-scatter diffraction, and electron microprobe were used to characterize the compositions and structures of these two minerals and associated phases.

Occurrence, Chemistry, and Crystallography: Thortveitite [$(Sc_{1.60}Zr_{0.13}Ti_{0.08}Mg_{0.06}Y_{0.04}Fe_{0.04}Ca_{0.02})(Si_{1.91}Ti_{0.08}Al_{0.01})O_7$] occurs with davisite (15 wt% Sc_2O_3), panguite [$(Ti_{0.71}Sc_{0.40}Al_{0.24}Mg_{0.14}Si_{0.08}Fe_{0.06}Zr_{0.05}Cr_{0.05}Ca_{0.05}Y_{0.03})_{\sum 1.82}O_3$], and MgAl-spinel. These phases form clots that are in 2-D mostly or entirely enclosed in Sc-bearing diopside (3–8 wt% Sc_2O_3). There is a step function in composition between davisites and the diopside where in contact. Panguite appears as irregular grains, 0.5–2 μm in size, along with fine-grained spinel within davisite or serpentinized regions, presumably after davisite. The thortveitite is subhedral, 1.5×3.5 μm to 6.5×9.0 μm, and is in contact with davisite/alteration or diopside. Where in contact with davisite, thortveitite often appears embayed, suggestive of a reaction relationship. Thortveitite appears to be inclusion free.

Origin and Significance: With the discovery of thortveitite, the Sc-, Zr-rich menagerie in carbonaceous chondrites now includes thortveitite, panguite, davisite, allendeite ($Sc_4Zr_3O_{12}$) [3], tazheranite (Sc- and/or Y-stabilized cubic zirconia) [3, 4], and lakargiite ($CaZrO_3$) [5]. MUR1 contains three of these Sc-enriched phases, thortveitite, panguite and davisite. Texturally, thortveitite formed first in MUR1, possibly with later partial reaction with vapor (?) to form davisite + spinel + panguite. Molar Sc/Zr of MUR1 thortveitite (approximately 12) is intermediate between davisite (approximately 15) and panguite (approximately 9), consistent with conservation of Sc/Zr in a reaction between thortveitite and vapor (source of Ti, Ca, Mg, and Al) to produce davisite + panguite + spinel. Since Sc/Zr in all of these Sc-, Zr-bearing phases are much higher than solar (1.2), prior fractionation of a separate Zr-rich phase may be indicated. Further work is required to determine MUR1's place in the nebular framework but, if the thorveitite is an early condensate, it may well be the first silicate and it certainly is more refractory than melilite. Indeed, davisite, which appears to be a reaction product of thortveitite in MUR1, may also predate melilite.

References: [1] Ebel D. S. and Grossman L. 2000. *Geochimica et Cosmochimica Acta* 64:339–366. [2] Ma C. et al. 2011. Abstract #1276. 42nd Lunar and Planetary Science Conference. [3] Ma C. et al. 2009. Abstract #1402. 40th Lunar and Planetary Science Conference. [4] Ma C. and Rossman G. R. 2008. *Geochimica et Cosmochimica Acta* 72:12S, A577. [5] Ma C. 2011. 74th Annual Meeeting of the Meteoritical Society. Abstract #5169.